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**(54)** **Suds suppressor compositions and their use in detergent compositions.**

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**EP 0 142 910 B1**

## Description

This invention relates to suds-suppressor compositions and to use thereof in detergent compositions. In particular, it relates to heavy duty detergent compositions having controlled sudsing characteristics especially when used in automatic washing machines for washing clothes and the like.

Detergent compositions normally contain surfactants which tend to produce foam when agitated in aqueous solution. For many applications, especially in automatic washing and dishwashing machines, excess foam production is a serious problem and with many effective surfactants, it is necessary to add foam suppressing or controlling agents in order to prevent suds-overflow from the machine or under-usage of product by the user. On the other hand, consumers normally expect and prefer a certain amount of foam to be present and, indeed, research has shown that consumers are highly sensitive to a reduction in the foam level pattern. In any particular application, therefore, the optimum degree of foaming will be sufficiently low to avoid oversudsing under all conceivable washing machine temperatures, load and soil conditions, but sufficiently high to meet the consumers preference for a moderate to generous level of foam.

Detergent compositions currently sold for the European domestic automatic washing machine market generally contain up to about 12% of organic surfactant and for such compositions, suds-suppressors satisfying the above constraints are now well established. For example, in EP—A—46342, it is taught to use a polydimethylsiloxane/hydrophobic silica suds-suppressor in the form of a dispersion in an ethoxylated nonionic surfactant using certain siloxane-oxyalkylene copolymers as dispersing agent. In EP—A—8829, a suds-suppressor is disclosed consisting of a major portion of wax together with a nonionic dispersing agent and hydrophobic silica. GB—A—1,407,977 discloses protection of a polydimethylsiloxane/silica suds-suppressor in a water-soluble dispersible carrier.

In detergent compositions containing a high level of surfactant, however, (in excess of about 12%) problems of foam control in front-loading automatic washing machines become increasingly intractable. Thus, the technique of dispersing polydimethylsiloxane/silica in nonionic surfactant is found to become impractical at high levels of suds-suppressor because of diminishing dispersion stability. The wax/silica/dispersant systems are also found to be deficient because of their inherently slow kinetics; in other words, the rate of release of wax/silica fails to match the rate of transport of surfactant to the air/water interface. Conventional polydimethylsiloxane/silica suds-suppressors are also deficient for foam control in high active detergent compositions, presumably because the polydimethylsiloxane is rapidly dispersed or solubilized by the higher surfactant levels. Furthermore, these problems of foam control are found to be greatly exacerbated in concentrated surfactant systems containing C<sub>10-16</sub> anionic or cationic surfactants which are known to have strong foam-generating characteristics.

The present invention thus provides a suds-suppressor composition suitable for addition to a high active heavy duty detergent composition to provide improved foam control characteristics. It further provides a detergent composition containing a high level of organic surfactant and having improved foaming characteristics across the range of wash temperature conditions. It also provides a high active detergent composition containing C<sub>10-16</sub> anionic and/or cationic surfactants and having improved foaming characteristics under varying wash temperature, product usage, soil, load and rinsing conditions.

According to the present invention, there is provided a suds-suppressor composition comprising:  
(a) a suds suppressor system comprising a blend of

- (i) a high shear mix of polydimethylsiloxane and hydrophobic silica suds suppressing agents in a weight ratio of polydimethylsiloxane:hydrophobic silica in the range from 75:25 to 99:1, the polydimethylsiloxane having a viscosity at 25°C in the range from 20 to 12,500 mm<sup>2</sup>s<sup>-1</sup>, and
- (ii) polydimethylsiloxane suds suppressing agent having a viscosity at 25°C of at least 25,000 mm<sup>2</sup>s<sup>-1</sup> wherein the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least 18,000 mm<sup>2</sup>s<sup>-1</sup>, the suds suppressor system being dispersed in:

(b) a water-soluble or water-dispersible organic carrier comprising:

- (i) from 1% to 100% by weight thereof of a first organic carrier component having a melting point in the range from 38°C to 90°C, and
- (ii) from 0% to 99% by weight thereof of a second organic carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from 9.5 to 13.5 and a melting point in the range from 5°C to 36°C.

The suds suppressor composition thus comprises a blend of two polydimethylsiloxane components, the first component being a high shear mix of polydimethylsiloxane and hydrophobic silica wherein the polydimethylsiloxane has a viscosity of from 20 to 12,500 mm<sup>2</sup>s<sup>-1</sup>, and the second component being polydimethylsiloxane having a viscosity of at least 25,000 mm<sup>2</sup>s<sup>-1</sup>. The high shear mix is preferably a mixture of polydimethylsiloxane having a viscosity in the range from 100 to 4,000 mm<sup>2</sup>s<sup>-1</sup> preferably from 500 to 2000 mm<sup>2</sup>s<sup>-1</sup> with hydrophobic silica in a weight ratio of from 80:20 to 95:5. The high viscosity polydimethylsiloxane preferably has a viscosity of at least 30,000 mm<sup>2</sup>s<sup>-1</sup>, more preferably from 50,000 to

100,000  $\text{mm}^2\text{s}^{-1}$ . The blend of high shear mix and high viscosity polydimethylsiloxane, on the other hand, has a viscosity of at least 18,000  $\text{mm}^2\text{s}^{-1}$  preferably at least 20,000  $\text{mm}^2\text{s}^{-1}$ , more preferably from 25,000 to 60,000  $\text{mm}^2\text{s}^{-1}$ . The high shear mix and high viscosity silicone are generally blended in a weight ratio of from 4:1 to 1:4, more preferably from 2:1 to 1:2.

The hydrophobic silica component of the high shear mix preferably has a particle size of not more than 100 nm, more preferably from 10 to 20 nm and a specific surface area above 50  $\text{m}^2/\text{g}$ . The hydrophobic silica can be made, for example, by reacting fumed silica with a trialkyl chlorosilane (i.e. "silanated") to affix hydrophobic trialkylsilane groups on the surface of the silica. The hydrophobic silica is then high shear mixed with polydimethylsiloxane, the latter being end-blocked generally with trimethylsilyl or hydroxyl groups. The polydimethylsiloxane can be prepared by various techniques such as the hydrolysis and subsequent condensation of dimethyldihalosilanes, or by the cracking and subsequent condensation of dimethylcyclotrisiloxanes.

The high shear mix can be prepared using any conventional high shear mixing equipment. Preferably, however, mixing is performed using an in-line high shear recirculation pump such as supplied by Janke and Kunkel. In practice, the hydrophobic silica is initially dispersed in the polydimethylsiloxane in a reservoir under low shear conditions using, for example a paddle mixer, and the dispersion is then continuously drawn-off and circulated via the high shear pump back into the reservoir until bulk homogeneity is achieved. Shear conditions in the pump are generally such that in a single pass, the temperature of the dispersion leaving the pump is raised from ambient to a temperature in excess of 95°C, preferably in excess of 110°C. Although a single pass under high shear turbulent flow conditions is normally adequate, nevertheless, to achieve bulk homogeneity mixing is generally continued until the temperature of the dispersion in the reservoir itself exceeds 95°C. The viscosity of the dispersion also rises to some extent during the high shear mixing step. Thus in preferred embodiments employing polydimethylsiloxane of viscosity from 500  $\text{mm}^2\text{s}^{-1}$  to 2000  $\text{mm}^2\text{s}^{-1}$ , high shear mixing raises the viscosity into the range from 6000 to 10,000  $\text{mm}^2\text{s}^{-1}$ .

The suds-suppressor compositions of the invention comprise the suds-suppressor system in the form of a dispersion in a water-soluble or water-dispersible organic carrier. The carrier comprises from 1% to 100% of a first carrier component having a melting point in the range from 38°C to 90°C, preferably from 38°C to 60°C, more preferably from 40°C to 55°C, and from 0% to 99% of a second carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from 9.5 to 13.5 and a melting point in the range from 5°C to 36°C. The weight ratio of the first organic carrier component to suds-suppressor system is preferably from 10:1 to 1:5, more preferably from 4:1 to 1:2, most preferably from 2:1 to 1:1. A preferred first organic carrier component comprises ethoxylated nonionic surfactant having an HLB in the range from 15 to 19, preferably from 17 to 19. Suitable nonionic surfactants are the condensation products of the primary or secondary alcohols having from 15 to 24 carbon atoms, in either straight or branched chain configuration, with from 14 to 150, preferably from 20 to 100, more preferably from 35 to 100 moles of ethylene oxide per mole of aliphatic alcohol. Examples of surfactants of this type are the condensation products of hardened tallow alcohol with an average of between 20 and 100 moles, preferably about 80 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Other suitable organic carriers include polyethyleneglycols having a molecular weight of from 400 to 40,000, preferably from 1500 to 10,000,  $\text{C}_{12-24}$  fatty acids and esters thereof, polyvinylpyrrolidone of molecular weight in the range from 40,000 to 700,000 and mixtures thereof. In the case of mixtures, however, the first organic carrier component preferably comprises at least 35%, more preferably at least 45% of ethoxylated nonionic surfactant in order to promote transport of suds suppressor to the air/water interface.

The melting point of the organic carrier components is taken herein to refer to the temperature at which melting is completed. Conveniently this temperature can be determined by thermal analysis using a Dupont 910 Differential Scanning Calorimeter with Mechanical Cooling Accessory and R90 Thermal Analyser as follows. A 5—10 mg sample of the material containing no free water or solvent, is encapsulated in a hermetically sealed pan with an empty pan as reference. The sample is initially heated until molten and then rapidly cooled (at about 20—30°C/min) to -70°C. Thermal analysis is then carried out at a heating rate of 10°C/min using sufficient amplification of  $\Delta T$  signal (i.e. temperature difference between sample and reference-vertical axis) to obtain an endotherm-peak signal:baseline noise ratio of better than 10:1. The melting completion temperature is then the temperature corresponding to the intersection of the tangential line at the steepest part of the endotherm curve at the high temperature end of the endotherm, with the horizontal line, parallel to the sample temperature axis, through the highest temperature endotherm peak.

In preferred embodiments, the suds-suppressor compositions of the invention also comprise a siloxane-oxyalkylene copolymer dispersing agent which provides improved homogeneity of the polydimethylsiloxane and silica components within the organic carrier. The dispersing agent is generally added at a weight ratio with respect to polydimethylsiloxane of from 1:4 to 1:40, preferably from 1:6 to 1:20. The siloxane-oxyalkylene copolymer dispersing agent suitable for use herein has the general formula I:

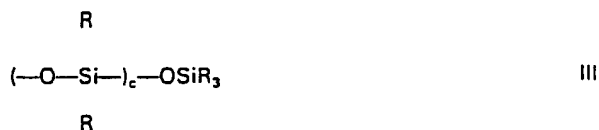


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wherein a is 0 or an integer from 1 to 3, R is an alkyl group, containing from 1 to 30 carbon atoms, or a group of formula II:

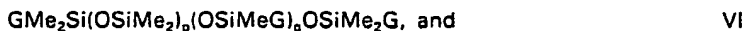


wherein R' is an alkylene group containing from 1 to 6 carbon atoms, b has a value of from 1 to 100, preferably from 10 to 30; and R'' is a capping group which can be selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:—



wherein R is as defined above and c has a value from 1 to 200; and wherein at least one R group in the compound has the formula II.

Preferred dispersing agents of the above type are selected from copolymers having the general formulae IV to VII:



wherein R''' is a C<sub>1-10</sub> alkyl group, Me is methyl, G is the group of formula II, a has a value of 0 or 1, p has a value of at least 1, q has a value of 0 to 50 and r has a value of 1 to 50. Preferred dispersants contain G groups in non-terminal positions and contain a mixture of oxyethylene and oxypropylene groups, particularly in about a 1:1 ratio. Highly preferred are dispersants of formula VII having p:r from 30 to 120 with the ratio p:r from 2:1 to 8:1.

The suds suppressor compositions of the invention are of two main types—a granular composition wherein the organic carrier consists essentially completely of the first carrier component; and a liquid or liquifiable composition wherein the organic carrier comprises from 1% to 50%, preferably from 2% to 25% of the first carrier component and from 50% to 99% preferably from 75% to 98% of the second carrier component. In the latter instance the first carrier component is critical for storage stability of the suds-suppressor composition.

The granular suds-suppressor composition herein preferably also comprises from 25% to 95% thereof, more preferably from 50% to 85% thereof of a solid water-soluble or dispersible inorganic diluent. Suitable inorganic diluents include alkali metal, alkaline earth metal and ammonium sulphates and chlorides, neutral and acid alkali metal carbonates, orthophosphates and pyrophosphates, and alkali metal crystalline and glassy polyphosphates. A preferred inorganic diluent is sodium tripolyphosphate. Suitable water-insoluble but dispersible diluents include the finely-divided natural and synthetic silicas and silicates, especially smectite-type and kaolinite-type clays such as sodium and calcium montmorillonite, kaolinite itself, aluminosilicates, and magnesium silicates and fibrous and microcrystalline celluloses.

In terms of processing, the granular suds-suppressor compositions are preferably made by forming a melt of the first organic carrier component, adding the high shear mix and the high viscosity silicone, preferably as a premix, to the melt, subjecting the melt to high shear mixing, adding the silicone-oxyalkylene copolymer dispersing agent, and agglomerating the melt with the inorganic diluent in, for example, a pan agglomerator, fluidized bed, Schugi mixer or the like. A preferred inorganic diluent is sodium tripolyphosphate. The particle size of the resulting agglomerate is preferably from 0.5 mm to 2 mm, especially from 0.84 to 1.4 mm. Critically, the high shear mix of polydimethylsiloxane and hydrophobic silica having a viscosity of from 20 to 12,500 mm<sup>2</sup>s<sup>-1</sup> must be preformed prior to admixture with high viscosity silicone.

The liquid or liquifiable suds suppressor compositions on the other hand, are preferably made by mixing the first and second organic carrier components and, if present, the siloxane-oxyalkylene copolymer dispersing agent, premixing the high shear mix and high viscosity silicone, and high shear mixing the premix with the organic carrier.

The granular suds-suppressor compositions of the invention are normally incorporated in a granular detergent composition at a level of from 0.1% to 10%, preferably from 0.5% to 5% by weight thereof. The liquid or liquifiable suds-suppressor compositions, on the other hand, are normally incorporated at a level

in the range from 0.5% to 30%, preferably from 3% to 20% by weight of composition. The detergent compositions herein generally contain in total from 3% to 60% preferably from 12% to 50%, more preferably from 14% to 30% of non-soap detergent, organic surfactant selected from anionic, nonionic, ampholytic, zwitterionic and cationic surfactants and mixtures thereof. Surfactants useful herein are listed in US-A-4,222,905 and US-A-4,239,659. Preferred detergent compositions comprise base granules constituting from 30% to 99.5% by weight of composition which in turn comprise from 3% to 30%, preferably from 5% to 20% by weight of composition of non-soap organic surfactant selected from anionic surfactants, cationic surfactants and mixtures thereof. The base granules will generally also contain a detergency builder as discussed below.

The anionic surfactant can be any one or more of the materials used conventionally in laundry detergents. Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulpho-carboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy alkane-1-sulphonate, and beta-alkyloxy alkane sulphonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from 8 to 22, especially from 10 to 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the  $C_{8-18}$ , preferably the  $C_{10-16}$  fatty alcohols and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from 9 to 15, especially 11 to 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in US-A-2,220,099 and US-A-2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is 11.8 carbon atoms, abbreviated as  $C_{11.8}$  LAS, and  $C_{12}-C_{15}$  methyl branched alkyl sulphates.

Other anionic detergent compounds herein include the sodium  $C_{10-18}$  alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphonates and sulphates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulphate containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts or esters of alpha-sulphonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulphonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulphates containing from 10 to 18, especially 10 to 16 carbon atoms in the alkyl group and from 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulphonates containing from 12 to 24, preferably from 14 to 16 carbon atoms, especially those made by reaction with sulphur trioxide followed by neutralization under conditions such that any sulfones present are hydrolysed to the corresponding hydroxy alkane sulphonates; water-soluble salts of paraffin sulphonates containing from 8 to 24, especially 14 to 16 carbon atoms, and beta-alkyloxy alkane sulphonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulfonate and sulfate surfactants in a weight ratio of from 5:1 to 1:5, preferably from 5:1 to 1:1, more preferably from 5:1 to 1.5:1. Especially preferred is a mixture of an alkyl benzene sulfonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulfate having from 10 to 16 carbon atoms in the alkyl radical or an ethoxy sulfate having from 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, the cation being an alkali metal, preferably sodium.

The nonionic surfactants useful in the present invention both as detergent and as the second organic carrier component are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 9.5 to 13.5, preferably from 10 to 12.5. The hydrophobic moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols

having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 13 moles of ethylene oxide.

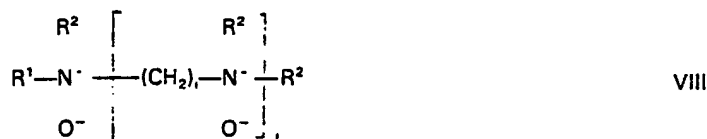
2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to 12 moles, preferably 2 to 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols (RTM), Dobanols (RTM) and Neodols (RTM) which have about 25% 2-methyl branching (Lutensol (RTM) being a Trade Name of BASF, Dobanol (RTM) and Neodol (RTM) being Trade Names of Shell), or Synperonics (RTM), which are understood to have about 50% 2-methyl branching (Synperonic (RTM) is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol (RTM) 45-4, Dobanol (RTM) 45-7, Dobanol (RTM) 45-9, Dobanol (RTM) 91-2.5, Dobanol (RTM) 91-3, Dobanol (RTM) 91-4, Dobanol (RTM) 91-6, Dobanol (RTM) 91-8, Dobanol (RTM) 23-6.5, Synperonic (RTM) 6, Synperonic (RTM) 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol (RTM) series having from 9 to 15 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic (RTM)" supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use herein are the  $C_9$ — $C_{15}$  primary alcohol ethoxylates containing 3—8 moles of ethylene oxide per mole of alcohol, particularly the  $C_{12}$ — $C_{15}$  primary alcohols containing 6—8 moles of ethylene oxide per mole of alcohol.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides.

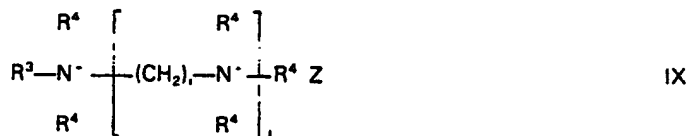
Suitable surfactants of the amine oxide class have the general formula VIII



wherein  $\text{R}^1$  is a linear or branched alkyl or alkenyl group having 8 to 20 carbon atoms, each  $\text{R}^2$  is independently selected from  $\text{C}_{1-4}$  alkyl and  $-(\text{C}_n\text{H}_{2n}\text{O})_m\text{H}$  where  $i$  is an integer from 1 to 6,  $j$  is 0 or 1,  $n$  is 2 or 3 and  $m$  is from 1 to 7, the sum total of  $\text{C}_n\text{H}_{2n}\text{O}$  groups in a molecule being no more than 7.

In a preferred embodiment  $\text{R}^1$  has from 10 to 16 carbon atoms and each  $\text{R}^2$  is independently selected from methyl and  $-(\text{C}_n\text{H}_{2n}\text{O})_m\text{H}$  wherein  $m$  is from 1 to 3 and the sum total of  $\text{C}_n\text{H}_{2n}\text{O}$  groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment,  $j$  is 0 and each  $\text{R}^2$  is methyl, and  $\text{R}^1$  is  $\text{C}_{12}$ — $\text{C}_{14}$  alkyl.

Suitable quaternary ammonium surfactants for use in the present composition can be defined by the general formula IX:



wherein  $\text{R}^3$  is a linear or branched alkyl, alkenyl or alkaryl group having 10 to 16 carbon atoms and each  $\text{R}^4$  is independently selected from  $\text{C}_{1-4}$  alkyl,  $\text{C}_{1-4}$  alkaryl and  $-(\text{C}_n\text{H}_{2n}\text{O})_m$  wherein  $i$  is an integer from 1 to 6,  $j$  is 0 or 1,  $n$  is 2 or 3 and  $m$  is from 1 to 7, the sum total of  $\text{C}_n\text{H}_{2n}\text{O}$  groups in a molecule being no more than 7, and wherein Z represents counteranion in number to give electrical neutrality.

In a preferred embodiment,  $\text{R}^3$  has from 10 to 14 carbon atoms and each  $\text{R}^4$  is independently selected

from methyl and  $(C_nH_{2n}O)_mH$  wherein  $m$  is from 1 to 3 and the sum total of  $C_nH_{2n}O$  groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment  $j$  is 0,  $R^4$  is selected from methyl, hydroxyethyl and hydroxypropyl and  $R^3$  is  $C_{12}$ — $C_{14}$  alkyl. Particularly preferred surfactants of this class include  $C_{12}$  alkyl trimethylammonium salts,  $C_{14}$  alkyltrimethylammonium salts, coconutalkyltrimethylammonium salts, coconutalkyldimethyl-hydroxyethylammonium salts, coconutalkyldimethylhydroxy-propylammonium salts, and  $C_{12}$  alkyldihydroxyethylmethyl ammonium salts.

As mentioned previously, the suds-suppressor compositions are particularly advantageous in detergent compositions containing a high level of deterative surfactant (at least 12%) wherein the surfactant is based completely or in part on anionic or cationic surfactants having from 10 to 16 carbon atoms. In preferred compositions therefore,  $C_{10}$ — $C_{18}$  anionic and/or cationic surfactants constitute from 5% to 100%, preferably from 10% to 50% by weight of the total deterative surfactant mixture.

In preferred embodiments, the detergent compositions of the invention also comprise from 0.2% to 3%, preferably from 0.5% to 1.5% of  $C_{16}$ — $C_{24}$  fatty acid or fatty acid soap. This acts in combination with the suds-suppressor system to provide improved suds-suppression robustness.

Suitable fatty acid soaps can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylammonium salts of fatty acids containing from 16 to 24 and preferably from 18 to 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from soybean oil, castor oil, tallow, whale and fish oils, grease, lard and mixtures thereof. The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil, as well as the free fatty acids themselves.

The detergent compositions of the invention can also contain up to 90%, preferably from 15% to 60% of detergency builder. Suitable detergent builders useful herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, sesquicarbonates, borates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates. "Seeded carbonate" builders as disclosed in BE—A—798,856 are also suitable.

Examples of suitable organic alkaline detergency builder salts are water-soluble polycarboxylate such as the salts of nitrilotriacetic acid, lactic acid, glycolic acid and ether derivatives thereof as disclosed in BE—A—821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propanetetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane cis,cis,cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetra-hydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetra-hydro-furan-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB—A—1,425,343.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA—A—755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphate.

A further class of builder is the insoluble alumino silicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation  $Na_z(AlO_2)_z(SiO_2)_y \cdot xH_2O$  wherein  $z$  and  $y$  are integers of at least 6, the molar ratio of  $z$  to  $y$  is in the range from 1.0 to 0.5 and  $x$  is an integer from 15 to 264. Compositions incorporating builder salts of this type form the subject of GB—A—1,429,143, DE—A—2,433,485, and DE—A—2,525,778.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate is preferably from 3% to 15%. Suitable silicate solids have a molar ratio of  $SiO_2$ /alkali metal in the range from 1.0 to 3.3, more preferably from 1.5 to 2.0.

The compositions of the invention can be supplemented by all manner of detergent and laundering components, inclusive of bleaching agents, enzymes, fluorescers, photoactivators, soil suspending agents, anti-caking agents, pigments, perfumes and fabric conditioning agents.

Enzymes suitable for use herein include those discussed in US—A—3,519,570 and US—A—3,533,139. Suitable fluorescers include Blankophor (RTM) MBBH (Bayer AG) and Tinopal (RTM) CBS and EMS (Ciba Geigy). Photoactivators are discussed in EP—A—57088, highly preferred materials being zinc phthalocyanine, tri- and tetra-sulfonates. Suitable fabric conditioning agents include smectite-type clays as disclosed in GB—A—1400898 and di- $C_{12}$ — $C_{24}$  alkyl or alkenyl amines and ammonium salts.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from the each other by not more than two carbon atoms. Polymers of this type are disclosed in GB—A—1,596,756.

Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl

ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

5 Peroxygen bleaching agents suitable for use in the present compositions include hydrogen peroxide, inorganic peroxides, peroxy salts and hydrogen peroxide addition compounds, and organic peroxides and peroxy acids. Organic peroxyacid bleach precursors (bleach activators) can additionally be present.

Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persulfate, urea-hydrogen peroxide addition products and the clathrate  
 10  $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot 1\text{NaCl}$ . Suitable organic bleaches include peroxyauric acid, peroxyoctanoic acid, peroxyundecanoic acid, peroxydecanoic acid, diperoxydodecanedioic acid, diperoxyazelaic acid, mono- and diperoxyphthalic acid and mono- and diperoxyisophthalic acid. Peroxyacid bleach precursors suitable herein are disclosed in GB—A—2040983, preferred being peracetic acid bleach precursors such as tetraacetylthylenediamine, tetraacetylthylenediamine, tetraacetylhexylenediamine, sodium p-  
 15 acetoxystyrene sulphonate, tetraacetylglucuril, pentaacetylglucose, octaacetylactose, and methyl O-acetoxystyrene benzoate. The higher acyl derivatives disclosed in EP—A—98129, published 11.01.84, and EP—A—0120591 published 03.10.84, are also highly suitable, especially the  $\text{C}_6$ — $\text{C}_{10}$  acyl oxybenzene sulphonates and carboxylates such as sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate. Bleach activators can be added at a weight ratio of bleaching agent to bleach activator in the range from 40:1 to  
 20 4:1.

In the Examples which follow, the abbreviations used have the following designations:—

LAS: Linear  $\text{C}_{11,8}$  alkyl benzene sulphonate.  
 TAE(n): Hardened tallow alcohol ethoxylated with n moles of ethylene oxide.  
 25 MAO:  $\text{C}_{12}$ — $\text{C}_{14}$  alkyl dimethylamine oxide.  
 AS:  $\text{C}_{12}$ — $\text{C}_{14}$  alcohol sulfate, sodium salt.  
 TAS: Tallow alcohol sulfate.  
 CATAB: Coconut alkyl trimethyl ammonium bromide.  
 Dobanol (RTM) 45-E-7: A  $\text{C}_{14-15}$  oxo-alcohol with 7 moles of ethylene oxide, marketed by Shell.  
 30 TAED: Tetraacetyl ethylene diamine.  
 Silicate: Sodium silicate having an  $\text{SiO}_2$ : $\text{Na}_2\text{O}$  ratio of 1.6:1.  
 Gantrez (RTM) AN119: Trade Name for maleic anhydride/vinyl methyl ether co-polymer, believed to have an average molecular weight of about 240,000, marketed by GAF. This was prehydrolysed with NaOH before addition.  
 35 MA/AA: Copolymer of 1:4 maleic acid/acrylic acid, average molecular weight about 80,000.  
 Brightener: Disodium 4,4'-bis(2-morpholino - 4 - anilino - s - triazino - 6 - ylaminostilbene - 2:2' - disulphonate).  
 Dequest (RTM) 2060: Trade Name for diethylenetriaminepenta(methylenephosphonic acid), marketed by Monsanto.  
 40 Dequest (RTM) 2041: Trade Name for ethylenediamine tetra(methylene phosphonic acid)monohydrate, marketed by Monsanto.  
 INOBS: Sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate.  
 Perborate: Sodium perborate tetrahydrate.  
 45 DC 198: Alkoxylated siloxane containing oxyethylene and oxypropylene groups, marketed by Dow Corning.  
 Silicone/silica: 85:15 by weight high shear mix of polydimethylsiloxane and silanated silica, particle size 10 to 20 nm, viscosity as indicated.  
 H.V. Silicone: Polydimethylsiloxane, viscosity 60,000  $\text{mm}^2\text{s}^{-1}$ .  
 50 Enzyme: Protease.

The present invention is illustrated by the following non-limiting examples:—

#### Examples I to V

55 Granular detergent compositions are prepared as follows. A base powder composition is first prepared by mixing the indicated components in a crutcher as an aqueous slurry at a temperature of about 80°C and containing about 35% water. The slurry is then spray dried at a gas inlet temperature of about 300°C to form base powder granules. Suds suppressor composition is then prepared by premixing the silicone/silica high shear mix and the high viscosity silicone, adding the premix to a melt of the ethoxylated tallow alcohol, adding the silicone/silica dispersing agent and spraying the dispersion onto sodium tripolyphosphate in a  
 60 fluidized bed. Finally, the base powder composition is dry mixed with suds suppressor, enzyme and bleach components, and additional nonionic surfactant and fatty acid, where present, are sprayed onto the total mixture.

All percentages are given by weight of total detergent composition.



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		Examples				
		I	II	III	IV	V
	Base powder					
5	LAS	6	4	10	5	8
	AS	4	2	2	5	—
	MAO	—	—	—	—	1
10	CATAB	—	—	2	—	1
	Gantrez (RTM) AN119	—	1	—	—	1
15	Silicate	6	7	5	5	10
	Sodium carbonate	—	8	—	13	5
	MA,AA	0.5	—	1	2	—
20	Brightener	0.2	0.3	0.1	0.2	0.2
	Dequest (RTM) 2060	—	—	0.3	—	—
25	Dequest (RTM) 2041	0.1	0.3	—	0.3	0.1
	EDTA	0.2	0.3	—	0.2	0.2
	Sodium tripolyphosphate	32	24	28	25	30
30	Magnesium sulphate (ppm)	1000	—	800	1000	1200
	Sodium sulphate, moisture & miscellaneous	to 100				
35	Suds suppressor					
	TAE(25)	0.6	0.37	0.5	—	—
	TAE(80)	—	—	—	0.72	0.7
40	PEG 6000	—	—	0.5	—	—
	H.V. Silicone	0.3	0.25	0.25	0.18	0.28
45	Silicone/silica (10,000 mm <sup>2</sup> s <sup>-1</sup> )	0.3	0.12	0.25	0.18	0.14
	DC198	0.05	0.03	0.08	0.04	0.06
	Sodium tripolyphosphate	1.75	1.55	3.42	1.88	2.32
50	Other additives					
	Enzyme	0.4	—	1.0	0.5	0.6
	Sodium perborate tetrahydrate	24	12	14	21	22
55	TAED	—	2	1	—	—
	INOBS	2	—	—	4	—
	Dobanol (RTM) 45-E-7	5	10	—	2	4
60	C <sub>18-22</sub> fatty acid	1	1.5	—	1	—

The above products combine excellent detergency performance together with improved foam regulation characteristics across the range of wash temperature, product usage, soil, load and rinsing conditions.

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## Examples VI to X

Granular detergent compositions are prepared as follows. Base powder compositions are first prepared as described in Examples I to V. Suds suppressor compositions are then prepared by mixing the first and second organic carrier components (TAE(80) and Dobanol (RTM) 45-E-7 respectively) together with the siloxane-oxyalkylene copolymer dispersing agent, premixing the silicone/silica high shear mix and the high viscosity silicone, high shear mixing the premix with the organic carrier component, dry mixing the base powder compositions with enzyme and bleach components and spraying the suds suppressor compositions onto the total dry mix.

All percentages are given by weight of total composition.

	VI	VII	Examples VIII	IX	X
Base powder					
LAS	5	12	7	10	5
TAS	5	1	—	1	1
Gantrez (RTM) AN119	—	1	—	0.8	1
Silicate	5	7	6	4	9
MA/AA	2	—	1	0.4	—
Brightener	0.2	0.3	0.1	0.5	0.2
Dequest (RTM) 2060	—	—	0.3	0.2	—
Dequest (RTM) 2041	0.3	0.3	—	—	0.1
EDTA	0.2	0.3	—	0.1	0.2
Sodium tripolyphosphate	23	24	32	32	30
Sodium carbonate	13	—	5	8	—
Magnesium sulphate (ppm)	1000	—	800	—	1200
Sodium sulphate, moisture & miscellaneous	to 100				
Suds suppressor composition					
Dobanol (RTM) 45-E-7	3.5	0.7	6	2	12
TAE (80)	0.5	0.5	1	0.4	1
DC-198	0.03	0.033	0.35	0.02	0.05
Silicone/silica (6,500 mm <sup>2</sup> s <sup>-1</sup> )	0.11	0.15	0.15	0.11	0.19
HV Silicone	0.22	0.15	0.2	0.11	0.38
Other additives					
Enzyme	0.6	—	1.2	—	0.9
Sodium perborate tetrahydrate	20	12	15	28	22
TAED	0.5	—	1	—	—
INOBS	2.5	—	—	3.5	—

The above products combine excellent detergency performance together with improved foam regulation characteristics across the range of wash temperature, product usage, soil, load and rinsing conditions.

## Claims

1. A suds suppressor composition characterized in that it comprises:

(a) a suds suppressor system comprising a blend of

- (i) a high shear mix of polydimethylsiloxane and hydrophobic silica suds suppressing agents in a weight ratio of polydimethylsiloxane:hydrophobic silica in the range from 75:25 to 99:1, the polydimethylsiloxane having a viscosity at 25°C in the range from 20 to 12,500 mm<sup>2</sup>s<sup>-1</sup>, and  
 (ii) polydimethylsiloxane suds suppressing agent having a viscosity at 25°C of at least 25,000 mm<sup>2</sup>s<sup>-1</sup> wherein the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least 18,000 mm<sup>2</sup>s<sup>-1</sup>, the suds suppressor system being dispersed in:

(b) a water-soluble or water-dispersible organic carrier comprising:

- (i) from 1% to 100% by weight thereof of a first organic carrier component having a melting point in the range from 38°C to 90°C, and  
 (ii) from 0% to 99% by weight thereof of a second organic carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from 9.5 to 13.5 and a melting point in the range from 5°C to 36°C.

2. A composition according to Claim 1 characterized in that the high shear mix is a mixture of polydimethylsiloxane having a viscosity at 25°C in the range from 100 to 4000 mm<sup>2</sup>s<sup>-1</sup> and hydrophobic silica in a weight ratio of from 80:20 to 95:5.

3. A composition according to Claim 1 or 2 characterized in that the high viscosity polydimethylsiloxane has a viscosity at 25°C of at least 30,000 mm<sup>2</sup>s<sup>-1</sup> preferably from 50,000 mm<sup>2</sup>s<sup>-1</sup> to 100,000 mm<sup>2</sup>s<sup>-1</sup> and the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least 20,000 mm<sup>2</sup>s<sup>-1</sup>, preferably from 25,000 mm<sup>2</sup>s<sup>-1</sup> to 60,000 mm<sup>2</sup>s<sup>-1</sup>.

4. A composition according to any of Claims 1 to 3 characterized in that the high shear mix and high viscosity polydimethylsiloxane are in a weight ratio of from 4:1 to 1:4, preferably from 2:1 to 1:2.

5. A composition according to any of Claims 1 to 4 characterized in that the first carrier component comprises an ethoxylated nonionic surfactant having an HLB in the range from 15 to 19, preferably from 17 to 19, and a melting point in the range from 38°C to 60°C, preferably from 40°C to 55°C.

6. A composition according to any of Claims 1 to 5 characterized in that it additionally comprises a siloxane-oxyalkylene copolymer dispersing agent having the general formula I

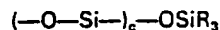


wherein a is 0 or an integer from 1 to 3, R is an alkyl group containing from 1 to 30 carbon atoms, or a group of formula II:



wherein R' is an alkylene group containing from 1 to 6 carbon atoms, b has a value of from 1 to 100; and R'' is a capping group which is selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:—

R



R

wherein R is as defined above and c has a value from 1 to 200; wherein at least one R group in the compound has the formula II; and wherein the weight ratio of dispersing agent to polydimethylsiloxane is from 1:4 to 1:40, preferably from 1:6 to 1:20.

7. A composition according to Claim 6 characterized in that the siloxane-oxyalkylene copolymer is selected from copolymers having the general formula IV to VII



wherein R''' is a C<sub>1-10</sub> alkyl group, Me is methyl, G is the group of formula II, a has a value of 0 or 1, p has a value of at least 1, q has a value of 0 to 50 and r has a value of 1 to 50.

8. A composition according to any of Claims 1 to 7 characterized in that the weight ratio of first carrier component:suds suppressor system is from 10:1 to 1:5.

9. A composition according to any of Claims 1 to 8 in granular form characterized in that the carrier consists essentially of the first carrier component.

10. A composition according to Claim 9 characterized additionally by from 25% to 95%, preferably from 50% to 85% thereof of a solid inorganic diluent.

11. A composition according to any of Claims 1 to 8 characterized in that the carrier comprises from 1% to 50%, preferably from 2% to 25% by weight thereof of the first carrier component, and from 50% to 99%, preferably from 75% to 98% by weight thereof of the second carrier component.

12. A granular detergent composition comprising

(a) from 3% to 60%, preferably from 12% to 50% by weight of non-soap, detergent, organic surfactant selected from anionic, nonionic, ampholytic, zwitterionic and cationic surfactants and mixtures thereof, characterized in that the composition additionally comprises:

(b) from 0.1 to 10%, preferably from 0.5 to 5% by weight of a granular suds suppressor composition according to Claim 9 or 10.

13. A granular detergent composition comprising

(a) from 30% to 99.5% by weight of base granules comprising from 3% to 30%, preferably from 5% to 20% by weight of the composition of non-soap organic surfactant selected from anionic and cationic surfactants and mixtures thereof, characterized in that the composition additionally comprises:

(b) from 0.5% to 30%, preferably from 3% to 20% by weight of a suds suppressor composition according to Claim 11 sprayed in fluent form onto at least a portion of the base granules.

14. A composition according to Claim 12 or 13 characterized in that the organic surfactant comprises a water-soluble C<sub>10-18</sub> alkyl, alkenyl or alkaryl anionic or cationic surfactant.

15. A composition according to any of Claims 12 to 14 characterized additionally by from 0.2% to 3%, preferably from 0.5% to 1.5% by weight of composition of C<sub>16</sub>—C<sub>24</sub> fatty acid or fatty acid soap.

### 30 Patentansprüche

1. Eine Schaumunterdrückerzusammensetzung, dadurch gekennzeichnet, daß sie umfaßt:

(a) ein Schaumunterdrückersystem, enthaltend eine Mischung aus

(i) einem unter Anwendung hoher Scherkräfte gebildeten Gemisch aus Polydimethylsiloxan-Schaumunterdrückungsmittel und hydrophobem Kieselsäure-Schaumunterdrückungsmittel in einem Gewichtsverhältnis von Polydimethylsiloxan:hydrophoben Kieselsäure im Bereich von 75:25 bis 99:1, wobei das Polydimethylsiloxan eine Viskosität bei 25°C im Bereich von 20 bis 12.500 mm<sup>2</sup> s<sup>-1</sup> aufweist, und

(ii) Polydimethylsiloxan-Schaumunterdrückungsmittel mit einer Viskosität bei 25°C von wenigstens 25.000 mm<sup>2</sup> s<sup>-1</sup>, wobei die Mischung aus unter Anwendung hoher Scherkräfte gebildetem Gemisch und hoch-viskosem Polydimethylsiloxan eine Viskosität bei 25°C von wenigstens 18.000 mm<sup>2</sup> s<sup>-1</sup> hat, und als Schaumunterdrückersystem in:

(b) einem wasserlöslichen oder wasserdispergierbaren organischen Träger dispergiert ist, der:

(i) 1 Gew.-% bis 100 Gew.-% desselben einer ersten organischen Trägerkomponente mit einem Schmelzpunkt im Bereich von 38°C bis 90°C, und

(ii) 0 Gew.-% bis 99 Gew.-% davon einer zweiten organischen Trägerkomponente, ausgewählt aus ethoxylierten, nichtionischen grenzflächenaktiven Mitteln mit einem Hydrophil-Lipophil-Gleichgewicht (HLB) im Bereich von 9,5 bis 13,5 und einem Schmelzpunkt im Bereich von 5°C bis 36°C, umfaßt.

2. Eine Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das unter Anwendung hoher Scherkräfte gebildete Gemisch eine Vermischung von Polydimethylsiloxan mit einer Viskosität bei 25°C im Bereich von 100 bis 4000 mm<sup>2</sup> s<sup>-1</sup> und hydrophober Kieselsäure in einem Gewichtsverhältnis von 80:20 bis 95:5 ist.

3. Eine Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das hoch-viskose Polydimethylsiloxan eine Viskosität bei 25°C von wenigstens 30.000 mm<sup>2</sup> s<sup>-1</sup>, vorzugsweise von 50.000 mm<sup>2</sup> s<sup>-1</sup> bis 100.000 mm<sup>2</sup> s<sup>-1</sup>, hat, und die Mischung aus unter Anwendung hoher Scherkräfte gebildetem Gemisch und hoch-viskosem Polydimethylsiloxan eine Viskosität bei 25°C von wenigstens 20.000 mm<sup>2</sup> s<sup>-1</sup>, vorzugsweise von 25.000 mm<sup>2</sup> s<sup>-1</sup> bis 60.000 mm<sup>2</sup> s<sup>-1</sup>, hat.

4. Eine Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das unter Anwendung hoher Scherkräfte gebildete Gemisch und das hoch-viskose Polydimethylsiloxan in einem Gewichtsverhältnis von 4:1 bis 1:4, vorzugsweise von 2:1 bis 1:2, vorliegen.

5. Eine Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die erste

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Trägerkomponente ein ethoxyliertes, nichtionisches grenzflächenaktives Mittel umfaßt, welches einen HLB-Wert im Bereich von 15 bis 19, vorzugsweise von 17 bis 19, und einen Schmelzpunkt im Bereich von 38°C bis 60°C, vorzugsweise von 40°C bis 55°C, hat.

6. Eine Zusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß sie zusätzlich ein Siloxan-Oxyalkylen-Copolymer-Dispergiermittel enthält, welches die allgemeine Formel I



hat, worin, a 0 oder eine ganze Zahl von 1 bis 3 ist, R eine Alkylgruppe mit 1 bis 30 Kohlenstoffatomen, oder eine Gruppe der Formel II:



ist, wobei R' eine 1 bis 6 Kohlenstoffatome enthaltende Alkylengruppe ist, b einen Wert von 1 bis 100 hat; und R'' eine abschließende Gruppe ist, die aus Wasserstoff, Alkyl-, Acyl-, Aryl-, Alkaryl-, Aralkyl- oder Alkenylgruppen mit bis zu 20 Kohlenstoffatomen, Sulfat-, Sulfonat-, Phosphat-, Carboxylat-, Phosphonat-, Borat- oder Isocyanatgruppen, oder Mischungen davon, ausgewählt ist; und Y eine Gruppe der Formel III:



ist, wobei R wie oben definiert ist, und c einen Wert von 1 bis 200 hat; wobei wenigstens eine R-Gruppe in der Verbindung die Formel II hat; und wobei das Gewichtsverhältnis von Dispergiermittel zu Polydimethylsiloxan 1:4 bis 1:40, vorzugsweise 1:6 bis 1:20, beträgt.

7. Eine Zusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß das Siloxan-Oxyalkylen-Copolymer aus Copolymeren der allgemeinen Formeln IV bis VII



ausgewählt ist, worin R''' eine C<sub>1-10</sub>-Alkenylgruppe ist, Me Methyl ist, G die Gruppe der Formel II ist, a einen Wert von 0 oder 1 hat, p einen Wert von wenigstens 1 hat, q einen Wert von 0 bis 50 hat, und r einen Wert von 1 bis 50 hat.

8. Eine Zusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß das Gewichtsverhältnis der ersten Trägerkomponente:Schaumunterdrückersystem 10:1 bis 1:5 beträgt.

9. Eine Zusammensetzung nach einem der Ansprüche 1 bis 8 in körniger Form, dadurch gekennzeichnet, daß der Träger im wesentlichen aus der ersten Trägerkomponente besteht.

10. Eine Zusammensetzung nach Anspruch 9, zusätzlich gekennzeichnet durch 25% bis 95%, vorzugsweise 50% bis 85%, derselben eines festen, anorganischen Verdünnungsmittels.

11. Eine Zusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der Träger 1 Gew.-% bis 50 Gew.-%, vorzugsweise 2 Gew.-% bis 25 Gew.-%, desselben an erster Trägerkomponente, und 50 Gew.-% bis 99 Gew.-%, vorzugsweise 75 Gew.-% bis 98 Gew.-%, desselben an zweiter Trägerkomponente enthält.

12. Eine körnige Detergensenzusammensetzung, enthaltend

(a) 3 Gew.-% bis 60 Gew.-%, vorzugsweise 12 Gew.-% bis 50 Gew.-%, deteratives, organisches, Nichtseifen-grenzflächenaktives Mittel, ausgewählt aus anionischen, nicht-ionischen, ampholytischen, zwitterionischen und kationischen grenzflächenaktiven Mitteln, sowie Gemischen davon, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich

(b) 0,1 bis 10 Gew.-%, vorzugsweise 0,5 bis 5 Gew.-%, einer körnigen Schaumunterdrückerzusammensetzung nach Anspruch 9 oder 10 enthält.

13. Eine körnige Detergensenzusammensetzung, enthaltend

(a) 30 Gew.-% bis 99,5 Gew.-% an Basiskörnern mit einem Gehalt von 3 Gew.-% bis 30 Gew.-%, vorzugsweise 5 Gew.-% bis 20 Gew.-%, der Zusammensetzung an organischem Nichtseifen-grenzflächenaktivem Mittel, ausgewählt aus anionischen und kationischen grenzflächenaktiven Mitteln, und Mischungen davon,

dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich

(b) 0,5 Gew.-% bis 30 Gew.-%, vorzugsweise 3 Gew.-% bis 20 Gew.-%, einer

Schaumunterdrückerzusammensetzung nach Anspruch 11 enthält, die in flüssiger Form auf wenigstens einen Teil der Basiskörner aufgesprüht worden ist.

14. Eine Zusammensetzung nach Anspruch 12 oder 13, dadurch gekennzeichnet, daß das organische grenzflächenaktive Mittel ein wasserlösliches, anionisches oder kationisches  $C_{10-16}$ -Alkyl-, Alkenyl- oder Alkaryl-grenzflächenaktives Mittel enthält.

15. Eine Zusammensetzung nach einem der Ansprüche 12 bis 14, zusätzlich gekennzeichnet durch 0,2 Gew.-% bis Gew.-%, vorzugsweise 0,5 Gew.-% bis 1,5 Gew.-%, der Zusammensetzung an  $C_{16-24}$ -Fettsäure oder Fettsäureseife.

#### Revendications

1. Composition antimousse caractérisée en ce qu'elle comprend:

(a) un système antimousse comprenant une combinaison

(i) d'un mélange à fort cisaillement d'agents antimousse de type polydiméthylsiloxane et silice hydrophobe, selon un rapport pondéral du polydiméthylsiloxane à la silice hydrophobe dans l'intervalle de 75:25 à 99:1, le polydiméthylsiloxane ayant une viscosité à 25°C dans l'intervalle de 20 à 12 500  $\text{mm}^2.\text{s}^{-1}$ , et

(ii) d'un agent antimousse de type polydiméthylsiloxane ayant une viscosité à 25°C d'au moins 25 000  $\text{mm}^2.\text{s}^{-1}$ , dans lequel la combinaison du mélange à fort cisaillement et du polydiméthylsiloxane de viscosité élevée a une viscosité à 25°C d'au moins 18 000  $\text{mm}^2.\text{s}^{-1}$ , le système antimousse étant dispersé dans:

(b) un véhicule organique hydrosoluble ou dispersable dans l'eau comprenant:

(i) de 1% à 100% en poids de ce mélange d'un premier constituant de véhicule organique ayant un point de fusion dans l'intervalle de 38°C à 90°C, et

(ii) de 0% à 99% en poids de ce mélange d'un second constituant de véhicule organique choisi parmi les tensioactifs non ioniques éthoxylés ayant un équilibre hydrophilelipophile (HLB) dans l'intervalle de 9,5 à 13,5 et un point de fusion de 5°C à 36°C.

2. Composition selon la revendication 1, caractérisée en ce que le mélange à fort cisaillement est un mélange d'un polydiméthylsiloxane ayant une viscosité à 25°C dans l'intervalle de 100 à 4 000  $\text{mm}^2.\text{s}^{-1}$  et de silice hydrophobe selon un rapport pondéral de 80:20 à 95:5.

3. Composition selon la revendication 1 ou 2, caractérisée en ce que le polydiméthylsiloxane de viscosité élevée a une viscosité à 25°C d'au moins 30 000  $\text{mm}^2.\text{s}^{-1}$ , de préférence de 50 000  $\text{mm}^2.\text{s}^{-1}$  à 100 000  $\text{mm}^2.\text{s}^{-1}$ , et la combinaison du mélange à fort cisaillement et du polydiméthylsiloxane de viscosité élevée a une viscosité à 25°C d'au moins 20 000  $\text{mm}^2.\text{s}^{-1}$ , de préférence de 25 000  $\text{mm}^2.\text{s}^{-1}$  à 60 000  $\text{mm}^2.\text{s}^{-1}$ .

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le mélange à fort cisaillement et le polydiméthylsiloxane de viscosité élevée sont en un rapport pondéral de 4:1 à 1:4, de préférence de 2:1 à 1:2.

5. Composition selon l'une quelconque des revendications 1 à 4, caractérisée en ce que le premier constituant de véhicule comprend un tensioactif non ionique éthoxylé ayant un HLB dans l'intervalle de 15 à 19, de préférence de 17 à 19, et un point de fusion dans l'intervalle de 38°C à 60°C, de préférence de 40°C à 55°C.

6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce qu'elle comprend en outre un agent dispersant de type copolymère siloxane-oxyalkylène répondant à la formule générale I



dans laquelle a est nul ou un nombre entier de 1 à 3, R est un groupe alkyle contenant 1 à 30 atomes de carbone ou un groupe de formule II:



dans laquelle R' est un groupe alkylène contenant de 1 à 6 atomes de carbone, b a une valeur de 1 à 100; et R'' est un groupe bloquant qui peut être choisi parmi un hydrogène, un groupe alkyle, acyle, aryle, alkylaryle, arylalkyle ou alcényle contenant jusqu'à 20 atomes de carbone, un groupe sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate ou isocyanate, ou leurs mélanges; Y est un groupe de formule III

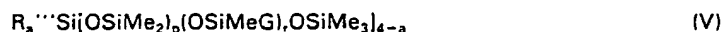
R



R

dans laquelle R est tel que défini ci-dessus et c a une valeur de 1 à 200; et dans laquelle au moins un groupe R, dans le compose, a pour formule II; et dans laquelle le rapport pondéral de l'agent dispersant au polydiméthylsiloxane est de 1:4 à 1:40, de préférence de 1:6 à 1:20.

7. Composition selon la revendication 6, caractérisée en ce que le copolymère siloxane-oxyalkylène est choisi parmi les copolymères répondant aux formules générales IV à VII:



dans lesquelles R''' est un groupe alkyle en C<sub>1</sub>—C<sub>10</sub>, Me est un groupe méthyle, G est le groupe de formule II, a a une valeur de 0 ou 1, p a une valeur d'au moins 1, q a une valeur de 0 à 50 et r a une valeur de 1 à 50.

8. Composition selon l'une quelconque des revendications 1 à 7, caractérisée en ce que le rapport pondéral du premier constituant de véhicule au système antimousse est de 10:1 à 1:5.

9. Composition selon l'une quelconque des revendications 1 à 8, sous forme granulaire, caractérisée en ce que le véhicule est essentiellement constituée du premier constituant de véhicule.

10. Composition selon la revendication 9, caractérisée en outre en ce qu'elle contient de 25% à 95%, de préférence de 50% à 85%, d'un diluant minéral solide.

11. Composition selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le véhicule comprend de 1% à 50%, de préférence de 2% à 25% de son poids, du premier constituant de véhicule, et de 50% à 99%, de préférence de 75% à 98% de son poids, du second constituant de véhicule.

12. Composition détergente granulaire comprenant:

(a) de 3% à 60%, de préférence de 12% à 50%, en poids d'un tensioactif organique détersif non saponacé choisi parmi les tensioactifs anioniques, non ioniques, ampholytes, zwitterioniques et cationiques, et leurs mélanges,

caractérisé en ce que la composition comprend en outre:

(b) de 0,1 à 10%, de préférence de 0,5 à 5%, en poids d'une composition antimousse granulaire selon la revendication 9 ou 10.

13. Composition détergente granulaire comprenant:

(a) de 30% à 99% du poids des granules de base comprenant de 3% à 30%, de préférence de 5% à 20%, du poids de la composition, d'un tensioactif organique non saponacé choisi parmi les tensioactifs anioniques et cationiques et leurs mélanges,

caractérisée en ce que la composition comprend en outre:

(b) de 0,5% à 30%, de préférence de 3% à 20%, en poids d'une composition antimousse selon la revendication 11, pulvérisée sous forme fluide sur au moins une partie des granules de base.

14. Composition selon la revendication 12 ou 13, caractérisée en ce que le tensioactif organique comprend un tensioactif anionique ou cationique hydrosoluble comportant un groupe alkyle, alcényle ou alkylaryle en C<sub>10</sub>—C<sub>16</sub>.

15. Composition selon l'une quelconque des revendications 12 à 14, caractérisée en outre en ce qu'elle comprend de 0,2% à 3%, de préférence de 0,5% à 1,5%, du poids de la composition, d'un acide gras en C<sub>16</sub>—C<sub>24</sub> ou d'un savon d'acide gras en C<sub>16</sub>—C<sub>24</sub>.